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(54) **Method for preparing PS plate.**

(57) A method for preparing a PS plate comprises the steps of treating an anodized aluminum plate with an aqueous solution of an alkali metal silicate having a pH ranging from 10 to 13 as determined at 25 °C, then treating the aluminum plate with an aqueous solution of an acid having a pH ranging from 1 to 6 and applying a light-sensitive layer onto the aluminum plate thus treated. The aluminum substrate of the PS plate is only slightly dissolved in an alkaline developer and this accordingly prevents the formation of insoluble compounds or sludge effectively, during development.

EP 0 565 006 A2

## BACKGROUND OF THE INVENTION

The present invention relates to a method for preparing a presensitized plate for use in making a lithographic printing plate.

5 A presensitized plate for use in making a lithographic printing plate (so-called PS plate) comprising an aluminum plate and a light-sensitive composition applied onto the plate in the form of a thin film is prepared by subjecting an aluminum plate to a surface-roughening treatment, for instance, a mechanical method such as brush graining or ball graining, an electrochemical method such as electrolytic graining, or a combination thereof to give a roughened surface; etching the surface with an aqueous solution of an acid or alkali; 10 anodizing the aluminum plate; optionally hydrophilizing the plate; and then applying a light-sensitive layer to the surface of the plate. This PS plate is in general imagewise exposed to light, developed, image-corrected and gummed up to give a lithographic printing plate which is then fitted to a printing press to carry out printing operations.

In the foregoing preparation of the PS plate, the anodization of the aluminum plate is carried out in 15 such a manner that any current does not pass through the back face thereof. However, the back face thereof is partially anodized since a part of the current passes therethrough. Moreover, it is believed that the back face of the aluminum plate should be anodized to some extent from the viewpoint of facilities for the bath of the anodization treatment and as a preventive measure against formation of scratch marks on the surface of the aluminum plate. For this reason, the aluminum plate used in the PS plate described above 20 has anodized layers on the surface and the back face.

The anodized layer is not soluble in a developer having a pH of less than 12.5, but soluble in a strong alkali developer having a pH of not less than 12.5. For this reason, the greater the quantity of the anodized layer formed on the surface and the back face of an aluminum plate, the greater the amount of the anodized layer dissolved in an alkali developer. The dissolved anodized layer is accumulated in the 25 developer and remains therein in the form of insoluble compounds or sludge. This in turn impairs the washing ability of an automatic developing machine and results in the deposition thereof on sensors for detecting, for instance, the activity of the developer through determination of an electric conductivity to thus interfere with the determination thereof. When the aluminum plate is treated with an aqueous solution of an alkali-metal silicate, the higher the molar ratio:  $\text{SiO}_2/\text{M}_2\text{O}$  (M represents an alkali-metal), the stronger the 30 foregoing tendency.

On the other hand, the aluminum plate is dissolved in a developer through the side on which a light-sensitive layer is applied, but the back face thereof is first dissolved therein and, therefore, if the time required for the development is short, the back face is dissolved in a higher ratio.

Moreover, there has been known a sealing treatment of an anodized layer through treatment with steam 35 for eliminating the phenomenon of remaining color on the side of the light-sensitive layer observed after the development thereof as disclosed in Japanese Patent Unexamined Publication (hereinafter referred to as "J.P. KOKAI") No. Hei 4-176690 (= EP-A-0485958). When the degree of the sealing is too high and the resulting lithographic printing plate is insufficiently desensitized, for instance, insufficiently gummed up, the hydrophilicity of non-image areas is impaired and are easily contaminated with printing inks. Thus, it has 40 been proposed that the steam-treatment should be carried out so that the degree of sealing ranges from 40 to 95% for the surface and, as disclosed in EP-A-0485958 not less than 80% for the back face. If the PS plate prepared using the aluminum plate thus treated is developed with an alkali developer having a pH of not less than 12.5, the amounts of insoluble compounds or sludge formed in the developer can be substantially reduced, but if the developing treatment is performed over a long period of time, insoluble 45 compounds or sludge are accumulated and adhered to the PS plates during processing.

On the other hand, the anodized layer is treated with an aqueous solution of an alkali silicate as disclosed in U.S. Patent No. 3,181,461, the anodized layer is only slightly dissolved in an alkali developer having a pH of not less than 12.5. However, the adhesion of the anodized layer of the aluminum plate thus 50 treated to a positive-working light-sensitive layer subsequently applied thereto is impaired and the printing durability of the resulting lithographic printing plate is substantially reduced, in particular, when a plate-cleaner is employed.

In addition, J.P. KOKAI No. Hei 2-185493 discloses a method for treating an anodized aluminum plate with an aqueous solution of an alkali metal silicate containing a hydroxide.

The anodized layer of an aluminum plate thus treated is scarcely dissolved in an alkaline developer 55 having a pH of 12.5 or higher, but the adhesion of the anodized layer of the aluminum plate thus treated to a positive-working light-sensitive layer subsequently applied is likewise impaired and the printing durability of the resulting lithographic printing plate is substantially reduced, in particular, when a plate-cleaner is employed.

## SUMMARY OF THE INVENTION

Accordingly, an object of the present invention is to provide a method for preparing a PS plate which permits the suppression of the dissolution of an anodized layer formed on an aluminum plate in an alkaline developer and in turn the reduction of the amounts of insoluble compounds or sludge formed in the developer and which can provide a lithographic printing plate exhibiting good adhesion between the aluminum substrate and a positive-working light-sensitive layer and satisfactory printing durability.

The inventors of this invention have conducted various studies to accomplish the foregoing object, have found out that the foregoing object can be achieved by treating an aluminum substrate with a specific alkali metal silicate solution and then with an acidic solution having a specific pH and thus have completed the present invention.

According to the present invention, the foregoing object can effectively be accomplished by providing a method for preparing a PS plate which comprises the steps of treating an anodized aluminum plate with an aqueous solution of an alkali metal silicate having a pH ranging from 10 to 13 as determined at 25 °C, then treating the aluminum plate with an aqueous solution of an acid having a pH ranging from 1 to 6 as determined at 25 °C and applying a light-sensitive layer onto the aluminum plate.

## DESCRIPTION OF THE PREFERRED EMBODIMENTS

The method of the present invention will be explained in more detail below.

Aluminum Plate

The aluminum plate used in the invention is a plate-like material of, for instance, pure aluminum or an aluminum alloy which comprises aluminum as a principal component and small amounts of trace elements.

Examples of the trace elements are silicon, iron, manganese, copper, magnesium, chromium, zinc, bismuth, nickel and titanium. Aluminum alloys usable in the invention comprise these trace elements in an amount of not more than 10% by weight. An aluminum material suitably used in the invention is pure aluminum, but the production of completely pure aluminum is difficult from the viewpoint of the aluminum refining technique and thus it is preferred to use those having contents of trace elements as low as possible. Aluminum alloys having a content of trace elements on the order of that defined above can be used in the invention without any trouble. As described above, the aluminum plate used in the invention is not restricted to those having specific compositions and any aluminum material known in the art and commonly used may appropriately be used in the invention. Examples of preferred aluminum materials are JIS A 1050, JIS A 1100, JIS A 1200, JIS A 3003, JIS A 3103 and JIS A 3005. The thickness of the aluminum plate used in the invention ranges from about 0.1 mm to 0.5 mm.

The aluminum plate is optionally degreased by treating it with an aqueous solution of a surfactant or an alkaline agent to remove rolling oils from the surface thereof and surface-grained prior to anodization.

Surface-Graining Treatment

Methods for surface-graining an aluminum plate include, for instance, a method for mechanically surface-roughening an aluminum plate, a method for electrochemically dissolving the surface of an aluminum plate and a method for selectively and chemically dissolving the surface of an aluminum plate. The mechanical surface-graining method usable in the invention may be any known method such as ball graining, brush graining, blast graining and buff graining methods. In addition, the electrochemical surface-graining methods include, for instance, those comprising electrolyzing the surface of an aluminum plate in an electrolyte such as a hydrochloric acid or nitric acid aqueous solution by passing an alternating or direct current through the aluminum plate. It is also possible to use a method comprising combination of these two kinds of methods as disclosed in J.P. KOKAI No. Sho 54-63902.

The aluminum plate thus surface-roughened is optionally etched with an alkali and neutralized.

Anodization Treatment

In the anodization treatment of an aluminum plate, any electrolyte may be used so far as they permit the formation of a porous oxidized layer on the aluminum plate, but electrolytes usable in general include aqueous solutions of, for instance, sulfuric acid, phosphoric acid, oxalic acid, chromic acid and mixture thereof and the concentrations of these electrolytes may be appropriately determined depending on the

kinds of electrolytes.

Conditions for anodization cannot unconditionally be determined since they vary depending on each particular electrolyte selected, but the anodization is desirably performed at an electrolyte concentration ranging from 1 to 80% by weight, an electrolyte temperature ranging from 5 to 70 °C, a current density ranging from 5 to 60 A/dm<sup>2</sup>, a voltage of from 1 to 100 V and an electrolyzation time of from 10 seconds to 50 minutes. Among these anodization methods, preferred are the method disclosed in U.K. Patent No. 1,412,768 in which an aluminum plate is anodized in a sulfuric acid solution at a high current density and the method disclosed in U.S. Patent No. 4,211,619 which comprises anodizing an aluminum plate in a sulfuric acid solution having a low concentration. The most preferred method comprises anodizing an aluminum plate in an electrolyte which comprises 5 to 20% by weight sulfuric acid and 3 to 15% by weight aluminum ions and which is maintained at a temperature ranging from 25 to 50 °C, using a direct current at a current density of 5 to 20 A/dm<sup>2</sup>.

The quantity of the anodized layer to be formed may be in the range of from 0.1 to 10 g/m<sup>2</sup>.

#### 15 Treatment with Alkali Metal Silicate

The foregoing anodized layer formed on the aluminum plate is treated by immersing the plate in an aqueous solution comprising 1 to 30% by weight, preferably 2 to 15% by weight of an alkali metal silicate and having a pH ranging from 10 to 13 as determined at 25 °C, at a desired temperature and time (for instance, 15 to 80 °C for 0.5 to 120 seconds).

If the pH of the alkali metal silicate aqueous solution is less than 10, the solution causes gelation, while if it exceeds 13.0, the oxidized layer is dissolved in the silicate solution.

Alkali metal silicates usable in the invention are, for instance, sodium silicate, potassium silicate and lithium silicate. Hydroxides used for increasing the pH of the alkali metal silicate aqueous solution include, for instance, sodium hydroxide, potassium hydroxide and lithium hydroxide.

The solutions used for the foregoing treatment may additionally contain alkaline earth metal salts or salts of Group IVB metals.

Examples of such alkaline earth metal salts include water-soluble salts, for instance, nitrates such as calcium nitrate, strontium nitrate, magnesium nitrate and barium nitrate, sulfates, hydrochlorides, phosphates, acetates, oxalates and borates.

Examples of salts of Group IVB metals include titanium tetrachloride, titanium trichloride, potassium titanium fluoride, potassium titanium oxalate, titanium sulfate, titanium tetraiodide, zirconium oxide chloride, zirconium dioxide, zirconium oxychloride and zirconium tetrachloride.

These alkaline earth metal silicates or salts of Group IVB metals may be used alone or in combination.

The amount of these metal salts to be added in the solution preferably ranges from 0.01 to 10% by weight and more preferably 0.05 to 5.0% by weight.

#### Treatment with Acidic Aqueous Solution

An acidic aqueous solution having a pH ranging from 1 to 6 as determined at 25 °C and used in the treatment performed after the treatment with an alkali metal silicate is an aqueous solution of an acid such as sulfuric acid, nitric acid, hydrochloric acid, oxalic acid or phosphoric acid.

If the pH of the treating solution is less than 1, the anodized layer is dissolved in the treating solution, while if it exceeds 6, any improvement of the adhesion between the aluminum plate and a light-sensitive layer subsequently applied cannot be anticipated. This treatment is suitably performed by immersing the plate in the solution at a temperature ranging from 10 to 70 °C for 0.5 to 120 seconds, and more preferably at a temperature ranging from 20 to 70 °C for 5 to 60 seconds.

A light-sensitive layer may directly be applied to the aluminum plate thus treated, but a hydrophilic underlying coating layer is optionally applied to the plate prior to the application of the light-sensitive layer.

#### Hydrophilic Underlying Coating Layer

Examples of hydrophilic underlying coating layer preferably used in the invention are a hydrophilic layer comprising a compound having at least one amino group and at least one member selected from the group consisting of carboxyl group and groups in the form of salts thereof as well as sulfo group and groups in the form of salts thereof as disclosed in J.P. KOKAI No. Sho 60-149491; a hydrophilic layer comprising a compound selected from the group consisting of those having at least one amino group and at least one hydroxyl group and salts thereof as disclosed in J.P. KOKAI No. Sho 60-232998; a phosphate-containing

hydrophilic layer as disclosed in J.P. KOKAI No. Sho 62-18494; a hydrophilic layer comprising a polymeric compound having, in the molecule, repeating units derived from at least one monomer having a sulfo group as disclosed in J.P. KOKAI No. Sho 59-101651; and an organic layer comprising at least one compound selected from the group consisting of substituted or unsubstituted aliphatic or aromatic compounds represented by the general formula:  $R^1(PO(OH)_2)_n$  or  $R^1(PO(OH)(R^2))_n$  (wherein  $n$  is 1 or 2; if  $n$  is 1,  $R^1$  and  $R^2$  each represents a substituted or unsubstituted alkyl, alkoxy, aryloxy, aryl, acyl or acyloxy group; and if  $n$  is 2,  $R^1$  represents a substituted or unsubstituted alkylene or arylene group and  $R^2$  is the same as that defined above) as disclosed in EP-A-0503602.

#### 10 Light-Sensitive Layer

A composition for the light-sensitive layer used in the invention may be any light-sensitive composition so far as it causes change in its solubility or swelling characteristics through exposure to light. Typical examples thereof will hereinafter be explained.

##### 15 (A) Light-Sensitive Layer Comprising o-Quinonediazide Compound

Light-sensitive compounds for positive-working light-sensitive compositions are, for instance, o-quinonediazide compounds and typical examples thereof include o-naphthoquinonediazide compounds.

20 Preferred examples of o-naphthoquinonediazide compounds include esters of 1,2-diazonaphthoquinonesulfonic acid chloride with pyrogallol-acetone resins as disclosed in Japanese Patent Publication for Opposition Purpose (hereinafter referred to as "J.P. KOKOKU") No. Sho 43-28403. Preferred examples of o-quinonediazide compounds include an ester of 1,2-diazonaphthoquinonesulfonic acid chloride with phenolformaldehyde resin as disclosed in U.S. Patent Nos. 3,046,120 and 3,188,210. Other useful o-naphthoquinonediazide compounds are known and disclosed in a variety of patents such as J.P. KOKAI Nos. Sho 47-5303, Sho 48-63802, Sho 48-63803, Sho 48-96575, Sho 49-38701 and Sho 48-13354; J.P. KOKOKU Nos. Sho 37-18015, Sho 41-11222, Sho 45-9610 and Sho 49-17481; U.S. Patent Nos. 2,797,213, 3,454,400, 3,544,323, 3,573,917, 3,674,495 and 3,785,825; U.K. Patent Nos. 1,227,602, 1,251,345, 1,267,005, 1,329,888 and 1,330,932; and German Patent No. 854,890.

30 It is also possible to use o-naphthoquinonediazide compounds prepared through the reactions of polyhydroxyl compounds having molecular weights of not more than 1,000 with 1,2-diazonaphthoquinonesulfonic acid chloride. Specific examples of these compounds are those disclosed in, for instance, J.P. KOKAI Nos. Sho 51-139402, Sho 58-150948, Sho 58-203434, Sho 59-165053, Sho 60-121445, Sho 60-134235, Sho 60-163043, Sho 61-118744, Sho 62-10645, Sho 62-10646, Sho 62-153950, Sho 62-178562 and Sho 64-76047; U.S. Patent Nos. 3,102,809, 3,126,281, 3,130,047, 3,148,983, 3,184,310, 3,188,210 and 4,639,406.

These o-naphthoquinonediazide compounds are synthesized by reacting polyhydroxyl compounds with 1,2-diazonaphthoquinonesulfonic acid chloride in an amount of preferably 0.2 to 1.2 eq. and more preferably 0.3 to 1.0 eq. per one hydroxyl group of the polyhydroxyl compound. Preferred 1,2-diazonaphthoquinonesulfonic acid chloride is 1,2-diazonaphthoquinone-5-sulfonic acid chloride, but 1,2-diazonaphthoquinone-4-sulfonic acid chloride may also be used.

40 The o-naphthoquinonediazide compound thus prepared comprises a mixture of those which differ, from one another, in positions of 1,2-diazonaphthoquinonesulfonic acid ester groups and the number of the ester groups introduced therein, but preferred are those having a rate of the compound whose hydroxyl groups are completely substituted with 1,2-diazonaphthoquinonesulfonic acid ester groups based on the mixture (the content of the compound completely esterified) of not less than 5 mole%, more preferably 20 to 99 mole%.

Positive-working light-sensitive compounds other than o-naphthoquinonediazide compounds include, for instance, o-nitrocarbinol ester group-containing polymeric compounds as disclosed in J.P. KOKOKU No. Sho 56-2696 which may likewise be used in the invention.

Also usable in the invention include, for instance, systems comprising combinations of photolytically acid-generating compounds with compounds having groups capable of causing dissociation by the action of acids such as -C-O-C- and -C-O-Si groups.

55 Examples of such systems include combinations of photolytically acid-generating compounds with acetal or O,N-acetal compounds as disclosed in J.P. KOKAI No. Sho 48-89003, with orthoester or amidoacetal compounds as disclosed in J.P. KOKAI No. Sho 51-120714, with polymers having acetal or ketal groups in the main chains as disclosed in J.P. KOKAI No. Sho 53-133429, with enol ether compounds as disclosed in J.P. KOKAI No. Sho 55-12995, with N-acyliminocarbon compounds as disclosed in J.P.

KOKAI No. Sho 55-126236, with polymers having orthoester groups in the main chains as disclosed in J.P. KOKAI No. Sho 56-17345, silyl ester compounds as disclosed in J.P. KOKAI No. Sho 60-10247 and with silyl ether compounds as disclosed in J.P. KOKAI Nos. Sho 60-37549 and Sho 60-121446.

The amount of these positive-working light-sensitive compounds (inclusive of the foregoing combinations) in the light-sensitive composition used in the invention suitably ranges from 10 to 50% by weight and more preferably 15 to 40% by weight on the basis of the total weight of the composition.

The o-quinonediazide compound by itself may form a light-sensitive layer, but the compound is preferably used in combination with an alkaline water-soluble resin as a binder. The light-sensitive composition may comprise a variety of alkaline water-soluble polymeric compounds. Such alkaline water-soluble resins are, for instance, novolak resins having the properties specified above and examples thereof include phenol-formaldehyde resins, cresol-formaldehyde resins such as m-cresol-formaldehyde resins, p-cresol-formaldehyde resins, m-/p-mixed cresol-formaldehyde resins and phenol-mixed cresol (m-, p- or m-/p-mixed cresol)-formaldehyde resins, phenol-modified xylene resins, polyhydroxystyrene, poly(halogenated hydroxystyrene), phenolic hydroxyl group-containing acrylic resins as disclosed in J.P. KOKAI No. Sho 51-34711, sulfonamido group-containing acrylic resins as disclosed in J.P. KOKAI No. Hei 2-866, and urethane resins. Among these alkali-soluble polymeric compounds, preferred are those having weight-average molecular weights ranging from 500 to 200,000 and number-average molecular weights ranging from 200 to 60,000.

The amount of these alkali-soluble polymeric compounds to be added to the composition is not more than 70% by weight on the basis of the total weight of the composition.

It is also preferred, for improving the ink-receptivity of images, to simultaneously use a condensate of a phenol carrying an alkyl group having 3 to 8 carbon atoms as a substituent with formaldehyde such as t-butylphenol-formaldehyde resin or octylphenol-formaldehyde resin or an o-naphthoquinone-diazidosulfonic acid ester of the condensate (such as those disclosed in J.P. KOKAI No. Sho 61-243446) as disclosed in U.S. Patent No. 4,123,279.

The light-sensitive composition used in the invention may further comprise cyclic acid anhydrides for improving the sensitivity of the composition, agents or compositions for obtaining visible images immediately after exposure to light, dyes for coloring images and/or other fillers. Examples of such cyclic acid anhydrides include, as disclosed in U.S. Patent No. 4,115,128, phthalic anhydride, tetrahydrophthalic anhydride, hexahydrophthalic anhydride, 3,6-endoxy- $\Delta^4$ -tetrahydrophthalic anhydride, tetrachlorophthalic anhydride, maleic anhydride, chloromaleic anhydride,  $\alpha$ -phenylmaleic anhydride, succinic anhydride and pyromellitic anhydride. The sensitivity of the composition can be increased by a factor of at most about 3 if these cyclic acid anhydrides are incorporated into the composition in an amount ranging from 1 to 15% by weight on the basis of the total weight of the composition. Typical examples of agents or compositions for obtaining visible images immediately after exposure to light are combinations of light-sensitive compounds capable of releasing acids through exposure to light with salt-forming organic dyes. Specific examples thereof are combinations of o-naphthoquinonediazido-4-sulfonic acid halides with salt-forming organic dyes as disclosed in J.P. KOKAI No. Sho 50-36209; and combinations of trihalomethyl compounds with salt-forming organic dyes as disclosed in J.P. KOKAI Nos. Sho 53-36223, Sho 54-74728, Sho 60-3626, Sho 61-143748, Sho 61-151644 and Sho 63-58440. Agents for coloring images may be the foregoing salt-forming organic dyes and other dyes. Preferred dyes (inclusive of the salt-forming organic dyes) may be oil-soluble dyes and basic dyes. Specific examples thereof are Oil Yellow #101, Oil Yellow #130, Oil Pink #312, Oil Green BG, Oil Blue BOS, Oil Blue #603, Oil Black BY, Oil Black BS, Oil Black T-505 (all of these are available from Orient Chemical Industries, Ltd.), Victoria Pure Blue, Crystal Violet (CI 42555), Ethyl Violet (CI 42600), Methyl Violet (CI 42535), Rhodamine B (CI 45170B), Malachite Green (CI 42000) and Methylene Blue (CI 52015). In addition, the dyes disclosed in J.P. KOKAI No. Sho 62-293247 are particularly preferred.

In the present invention, the light-sensitive composition is dissolved in a solvent capable of dissolving the foregoing every components and then applied to the surface of a substrate. Solvents usable herein include, for instance, ethylene dichloride, cyclohexanone, methyl ethyl ketone, ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, 2-methoxyethyl acetate, 1-methoxy-2-propanol, 1-methoxy-2-propyl acetate, toluene, ethyl acetate, methyl lactate, ethyl lactate, dimethylsulfoxide, dimethylacetamide, dimethylformamide, water, N-methylpyrrolidone, tetrahydrofurfuryl alcohol, acetone, diacetone alcohol, methanol, ethanol, isopropanol, diethylene glycol and dimethyl ether, which may be used alone or in combination. The concentration of the foregoing components (solid content) in the solution ranges from 2 to 50% by weight.

The amount of the composition to be applied varies depending on the applications of the composition, but in general it preferably ranges from 0.5 to 3.0 g/m<sup>2</sup> (as expressed in terms of solid content) for PS plates. The smaller the amount of the composition coated, the higher the sensitivity of the resulting light-sensitive film, but the lower the physical properties of the film.

The light-sensitive composition used in the invention may comprise surfactants for improving the coating properties thereof such as fluorine atom-containing surfactants as disclosed in J.P. KOKAI No. Sho 62-170950. The amount of the surfactant preferably ranges from 0.01 to 1% by weight and more preferably 0.05 to 0.5% by weight on the basis of the total weight of the light-sensitive composition.

#### (B) Light-Sensitive Layers Comprising Diazo Resins and Binders

Negative-working light-sensitive diazo compounds preferably used are condensed products (so-called light-sensitive diazo resins) of diphenylamine-p-diazonium salts, which are reaction products of diazonium salts with reactive carbonyl salt-containing organic condensation agents such as aldol or acetal, with formaldehyde as disclosed in U.S. Patent Nos. 2,063,631 and 2,667,415. Examples of other useful condensed diazo resins are disclosed in, for instance, J.P. KOKOKU Nos. Sho 49-48001, Sho 49-45322 and Sho 49-45323. These light-sensitive diazo resins are in general used in the form of water-soluble inorganic salts and, therefore, they can be applied in the form of aqueous solutions. Alternatively, these water-soluble diazo compounds can be reacted with aromatic or aliphatic compounds having at least one phenolic hydroxyl group or sulfonate residue or both of these groups according to the method disclosed in J.P. KOKOKU No. Sho 47-1167 to give substantially water-insoluble light-sensitive diazo resins as reaction products. The products can likewise be used in the invention.

It is also possible to use the foregoing diazo compounds in the form of reaction products with hexafluorophosphates or tetrafluoroborates as disclosed in J.P. KOKAI No. Sho 56-121031.

Examples of reactants having phenolic hydroxyl groups are hydroxybenzophenone, 4,4-bis(4'-hydroxyphenyl)pentanoic acid, resorcinol or diphenolic acids such as diresorcinol, which may have substituents. Specific examples of hydroxybenzophenones include 2,4-dihydroxybenzophenone, 2-hydroxy-4-methoxybenzophenone, 2,2'-dihydroxy-4,4'-dimethoxybenzophenone and 2,2',4,4'-tetrahydroxybenzophenone. Examples of preferred sulfonic acids include aromatic sulfonic acids such as sulfonic acids of benzene, toluene, xylene, naphthalene, phenol, naphthol and benzophenone or soluble salts thereof such as ammonium and alkali metal salts. These sulfonic acid residue-containing compounds may in general be substituted with lower alkyl groups, nitro group and/or an additional sulfonic acid group. Preferred examples thereof are benzenesulfonic acid, toluenesulfonic acid, naphthalenesulfonic acid, 2,5-dimethylbenzenesulfonic acid, sodium benzenesulfonate, naphthalene-2-sulfonic acid, 1-naphthol-2 (or 4)-sulfonic acid, 2,4-dinitro-1-naphthol-7-sulfonic acid, 2-hydroxy-4-methoxybenzophenone-5-sulfonic acid, sodium m-(p'-anilinophenylazo)benzenesulfonate, alizarinsulfonic acid, o-toluidine-m-sulfonic acid and ethanesulfonic acid. Sulfonic acids of alcohols and salts thereof are also useful in the invention. Generally, such compounds can easily be available as anionic surfactants and specific examples thereof include ammonium salts or alkali metal salts of, for instance, lauryl sulfate, alkylaryl sulfate, p-nonylphenyl sulfate, 2-phenylethyl sulfate and isooctylphenoxydiethoxyethyl sulfate.

These substantially water-insoluble light-sensitive diazo resins each is isolated by admixing an aqueous solution of a water-soluble diazo resin with an aqueous solution of the foregoing aromatic or aliphatic compound preferably in amounts approximately identical to one another in the form of precipitates.

In addition, diazo resins as disclosed in U.K. Patent No. 1,312,925 are likewise preferably used in the invention.

It is also preferred to use diazo resins having phosphorus atom-containing oxyacid groups as disclosed in J.P. KOKAI No. Hei 3-253857, diazo resins condensed with carboxyl group-containing aldehyde or acetal compounds thereof as disclosed in J.P. KOKAI No. Hei 4-18559, diazo resins co-condensed with carboxyl group-containing aromatic compounds such as phenoxyacetic acid as disclosed in J.P. KOKAI No. Hei 4-211253.

Most preferred diazo resins are, for instance, 2-methoxy-4-hydroxy-5-benzoylbenzenesulfonate of condensates of p-diazodiphenylamine with formaldehyde.

The content of these diazo resins in the light-sensitive layer suitably ranges from 5 to 50% by weight. The smaller the content of the diazo resin, the higher the light-sensitivity of the resulting light-sensitive layer, but the lower the stability thereof with time. The amount of the diazo resin most preferably ranges from about 8 to 20% by weight.

On the other hand, binders may be various kinds of polymeric compounds, but preferably used in the present invention include those comprising groups selected from hydroxyl, amino, carboxyl, amido, sulfonamido, active methylene, thioalcohol and/or epoxy groups. Examples of preferred binders include shellac as disclosed in U.K. Patent No. 1,350,521; polymers comprising, as main repeating units, those derived from hydroxyethyl acrylate or hydroxyethyl methacrylate as disclosed in U.K. Patent No. 1,460,973 and U.S. Patent No. 4,123,276; polyamide resins as disclosed in U.S. Patent No. 3,751,257; phenol resins

and polyvinyl acetal resins such as polyvinyl formal resins and polyvinyl butyral resins as disclosed in U.K. Patent No. 1,074,392; linear polyurethane resins as disclosed in U.S. Patent No. 3,660,097; phthalate-modified polyvinyl alcohol resins; epoxy resins obtained through condensation of bisphenol A and epichlorohydrin; amino group-containing polymers such as polyaminosulfone and polyalkylamino(meth)acrylate; and cellulose derivatives such as cellulose acetate, cellulose alkyl ether and cellulose acetate phthalate.

The composition comprising a diazo resin and a binder may further comprise other additives such as pH indicators as disclosed in U.K. Patent No. 1,041,463 and phosphoric acid and dyes as disclosed in U.S. Patent No. 3,236,646.

#### 10 (C) Light-Sensitive Layer Comprising Aside Compound and Binder (Polymeric Compound)

Examples of light-sensitive compositions of this kind include those comprising aside compounds and water-soluble or alkali-soluble polymeric compounds as disclosed in U.K. Patent Nos. 1,235,281 and 1,495,861 and J.P. KOKAI Nos. Sho 51-32331 and Sho 51-36128; and those comprising azido group-containing polymers and polymeric compounds as binders as disclosed in J.P. KOKAI Nos. Sho 50-5102, Sho 50-84302, Sho 50-84303 and Sho 53-12984.

#### (D) Other Light-Sensitive Resin Layer

20 Examples of other light-sensitive resins are polyester compounds as disclosed in J.P. KOKAI No. Sho 52-96696; polyvinyl cinnamate resins as disclosed in U.K. Patent Nos. 1,112,277, 1,313,390, 1,341,004 and 1,377,747; photo-polymerizable photopolymer compositions as disclosed in U.S. Patent Nos. 4,072,528 and 4,072,527.

#### 25 (E) Electrophotographic Light-Sensitive Layer

The electrophotographic light-sensitive layer mainly comprises a photoconductive compound and a binder, but may optionally comprise known dyes, pigments, chemical sensitizers and other additives for the improvement of the sensitivity and for imparting, to the layer, sensitivity to a desired wavelength range. The light-sensitive layer may comprise a single layer or a plurality of layers comprising those having a charge-generating function and those having a charge-transfer function. A lithographic printing plate can be obtained by forming a toner image on the light-sensitive layer according to the known electrophotographic process and then decoding the non-image areas while using the toner image as a resist layer. These light-sensitive layers are disclosed in various publications such as J.P. KOKOKU Nos. Sho 37-17162, Sho 38-6961, Sho 59-36259 and Sho 59-25217 and J.P. KOKAI Nos. Sho 56-107246, Sho 60-254142, Sho 56-146145, Sho 62-194257, Sho 57-147656, Sho 58-100862 and Sho 57-161863, all of which may be suitably used in the invention.

The thickness of the light-sensitive layer preferably ranges from 0.1 to 30  $\mu\text{m}$  and more preferably 0.5 to 10  $\mu\text{m}$ . The amount (solid content) of the light-sensitive layer to be applied to a substrate ranges from about 0.1 to about 7  $\text{g}/\text{m}^2$  and preferably 0.5 to 4  $\text{g}/\text{m}^2$ . The surface of the light-sensitive layer thus formed is preferably matted in order to shorten the evacuation time required for the close contact exposure in a vacuum printing frame and prevent an image from becoming indistinct. More specifically, such a mat layer can be formed by a method as disclosed in J.P. KOKAI No. Sho 50-12580 and J.P. KOKOKU Nos. Sho 57-6582 and Sho 61-28986 or a method as disclosed in J.P. KOKOKU No. Sho 62-62337 which comprises heat-fusing solid powder on the light-sensitive layer.

The PS plate of the present invention is imagewise exposed to light and then treated by the usual manner including development to give a lithographic printing plate.

For instance, a positive-working PS plate having a light-sensitive layer (A) is imagewise exposed to light and then developed with an alkaline aqueous solution such as those disclosed in U.S. Patent No. 4,259,434 and J.P. KOKAI No. Hei 3-90388 to remove the light-sensitive layer on the exposed area and to thus give a lithographic printing plate.

Alternatively, a negative-working PS plate having a light-sensitive layer (B) which comprises a diazo resin and a binder is imagewise exposed to light and then developed with a developer such as those disclosed in, for instance, U.S. Patent No. 4,186,006 to remove the light-sensitive layer on the unexposed area and to thus give a lithographic printing plate.

The PS plate of the invention can of course be subjected to the plate-making methods as disclosed in J.P. KOKAI Nos. Sho 54-8002, Sho 55-115045 and Sho 59-58431. More specifically, after developing the imagewise exposed PS plate, it is washed with water and then desensitized; or directly desensitized without



water-washing; or treated with an aqueous solution containing an acid; or desensitised after treating with an aqueous solution containing an acid. Moreover, in the development processing of the PS plate of this kind, the processing ability of an alkaline developer because the alkali concentration is reduced due to consumption thereof in proportion to the quantity of the PS plate processed or through absorption of air when an automatic developing machine is operated over a long time, but the processing ability of the alkaline developer can be recovered by the addition of a fresh developer (replenisher) or a replenisher having a high alkaline concentration as disclosed in J.P. KOKAI No. Sho 54-62004. In this case, the supplementation of the replenisher is preferably carried out by a method in which the replenisher is added in an amount proportional to the length of one side of the PS plate to be processed or the method disclosed in U.S. Patent No. 4,882,246.

Moreover, the foregoing plate-making process is preferably performed in an automatic developing machine as disclosed in J.P. KOKAI Nos. Hei 2-7054 and Hei 2-32357.

Furthermore, when erasing unnecessary portions of images after imagewise exposure, development, water-washing or rinsing the PS plate of the present invention, it is preferred to use an erasing solution as disclosed in J.P. KOKOKU No. Hei 2-13293. Desensitising gums optionally applied to the resulting lithographic printing plate at the final step of the plate-making process are preferably those disclosed in J.P. KOKOKU Nos. Sho 62-16834, Sho 62-25118 and Sho 63-52600 and J.P. KOKAI Nos. Sho 62-7595, Sho 62-11693 and Sho 62-83194.

In addition, when the PS plate of the present invention is subjected to burning-in treatment after imagewise exposure, development, water-washing or rinsing, optional erasing and water-washing, it is preferred to treat the plate with a surface-conditioning solution as disclosed in J.P. KOKOKU Nos. Sho 61-2518 and Sho 55-28062 and J.P. KOKAI Nos. Sho 62-31859 and Sho 61-159655, prior to the burning-in treatment.

The aluminum substrate of the PS plate of the present invention is only slightly dissolved in an alkaline developer and this accordingly prevents the formation of insoluble compounds or sludge effectively, during development.

The present invention will hereinafter be explained in more detail with reference to the following non-limitative working Examples. In addition, the effects practically achieved by the invention will also be discussed in detail while comparing with Comparative Examples. In the following Examples, the term "%" means "% by weight" unless otherwise specified.

#### Example 1

A JIS 1050 aluminum sheet was surface-grained with an aqueous suspension of pumice stone as an abrasive and a rotary nylon brush. At this stage, the surface roughness of the aluminum sheet was determined and found to be  $0.5 \mu$  (expressed in terms of central line-average surface roughness). After water-washing, the aluminum sheet was etched by immersing it in a 10% aqueous caustic soda solution heated up to  $70^\circ\text{C}$  to such an extent that the amount of dissolved aluminum was reached  $6 \text{ g/m}^2$ . After water-washing, the sheet was neutralized by immersing in a 30% nitric acid aqueous solution for one minute and then sufficiently washed with water. Thereafter, the sheet was electrolytically surface-roughened for 20 seconds in a 0.7% nitric acid aqueous solution using a rectangular alternating waved voltage having an anodic voltage of 13 V and a cathodic voltage of 6 V, then immersed in a 20% sulfuric acid solution maintained at  $50^\circ\text{C}$  to wash the surface thereof and washed with water.

Further a porous anodized layer was formed on the sheet in a 20% aqueous sulfuric acid solution using a direct current.

The aluminum sheet was electrolyzed at a current density of  $5 \text{ A/dm}^2$  while adjusting the electrolyzation time such that the weight of the anodized layer formed on the surface of the aluminum sheet was  $2.5 \text{ g/m}^2$  and the weight of the anodized layer formed on the back face thereof was  $0.5 \text{ g/m}^2$ , to thus give a substrate (I).

The substrate (I) was treated with a 10% aqueous sodium silicate solution (pH 11.2) at  $70^\circ\text{C}$  for 12 seconds, washed with water and then treated with an aqueous sulfuric acid solution having a pH of 2 at  $30^\circ\text{C}$  for 15 seconds.

The following light-sensitive composition was applied onto the substrate thus prepared so that the coated amount thereof was  $2.5 \text{ g/m}^2$  (weighed after drying) and then dried to form a light-sensitive layer.

Light-Sensitive Composition	
Component	Amount (g)
5 ester compound of naphthoquinone-1,2-diazo-5-sulfonyl chloride and pyrogallol-acetone resin (the compound disclosed in Example 1 of U.S. Patent No. 3,635,709)	0.75
cresol-novolak resin	2.00
Oil Blue #603 (available from Orient Chemical Industries, Ltd.)	0.04
10 ethylene dichloride	16
2-methoxyethyl acetate	12

The PS plate thus prepared was exposed to light from a 3 KW metal halide lamp for 50 seconds at a distance of 1 m through a transparent positive film in a vacuum printing frame and then developed with a 3.5% aqueous solution of sodium silicate (pH 12.9) having a molar ratio,  $\text{SiO}_2/\text{Na}_2\text{O}$ , of 0.83.

After the development, the plate was sufficiently washed with water, followed by a gumming up treatment and printing operation in the usual manner. In this respect, after processing 10 m<sup>2</sup> of the PS plate per one liter of the developer, the degree of dissolution of the anodized layer in the developer was evaluated on the basis of the condition of the insoluble compounds remaining in the developer. The results thus obtained and the printing durability are summarized in the following Table 1.

#### Example 2

The substrate (I) was treated with a 10% by weight aqueous solution of sodium silicate (pH 11.2) at 70 °C for 12 seconds, then washed with water and treated with an aqueous sulfuric acid solution having a pH of 2 at 30 °C for 15 seconds.

Thereafter, the same procedures used in Example 1 were repeated except that a solution comprising 1 g of phenylsulfonic acid, 39 g of water and 60 g of methanol was applied onto the substrate thus treated in an amount of 20 mg/m<sup>2</sup> (weighed after drying) and then dried at 80 °C for 30 seconds.

After processing 10 m<sup>2</sup> of the resulting PS plate per one liter of the developer, the developer was examined on whether insoluble compounds remained therein or not. The results thus obtained and the printing durability are summarized in the following Table 1.

#### Example 3

The same procedures used in Example 1 were repeated except that the substrate (I) was treated with a 10% by weight aqueous solution of sodium silicate (PM 13.0), to which sodium hydroxide was added, at 70 °C for 12 seconds, then washed with water and treated with an aqueous sulfuric acid solution having a pH of 2 at 30 °C for 15 seconds.

After processing 10 m<sup>2</sup> of the resulting PS plate per one liter of the developer, the developer was examined on whether insoluble compounds remained therein or not. The results thus obtained and the printing durability are summarized in the following Table 1.

#### Example 4

The substrate (I) was treated with a 10% by weight aqueous solution of sodium silicate (pH 13.0), to which sodium hydroxide was added, at 70 °C for 12 seconds, then washed with water and treated with an aqueous sulfuric acid solution having a pH of 2 at 30 °C for 15 seconds. Thereafter, the same procedures used in Example 1 were repeated except that a solution comprising 1 g of phenylphosphonic acid, 39 g of water and 60 g of methanol was applied onto the substrate thus treated in an amount of 20 [mg/m<sup>2</sup>] (weighed after drying) and then dried at 80 °C for 30 seconds.

After processing 10 m<sup>2</sup> of the resulting PS plate per one liter of the developer, the developer was examined on whether insoluble compounds remained therein or not. The results thus obtained and the printing durability are summarized in the following Table 1.

## Comparative Example 1

The same procedures used in Example 1 were repeated using the substrate (I) except that the treatments with an alkali metal silicate aqueous solution and with an aqueous sulfuric acid solution were omitted.

After processing 10 m<sup>2</sup> of the resulting PS plate per one liter of the developer, the developer was examined on whether insoluble compounds remained therein or not. The results thus obtained and the printing durability are summarized in the following Table 1.

## 10 Comparative Example 2

The same procedures used in Example 1 were repeated using the substrate (I) except that the treatment with an aqueous sulfuric acid solution were omitted.

After processing 10 m<sup>2</sup> of the resulting PS plate per one liter of the developer, the developer was examined on whether insoluble compounds remained therein or not. The results thus obtained and the printing durability are summarized in the following Table 1.

## Comparative Example 3

20 The same procedures used in Example 2 were repeated using the substrate (I) except that the treatment with an aqueous sulfuric acid solution were omitted.

After processing 10 m<sup>2</sup> of the resulting PS plate per one liter of the developer, the developer was examined on whether insoluble compounds remained therein or not. The results thus obtained and the printing durability are summarized in the following Table 1.

## 25 Comparative Example 4

The same procedures used in Example 3 were repeated using the substrate (I) except that the treatment with an aqueous sulfuric acid solution were omitted.

30 After processing 10 m<sup>2</sup> of the resulting PS plate per one liter of the developer, the developer was examined on whether insoluble compounds remained therein or not. The results thus obtained and the printing durability are summarized in the following Table 1.

## Comparative Example 5

35 The same procedures used in Example 4 were repeated using the substrate (I) except that the treatment with an aqueous sulfuric acid solution were omitted.

After processing 10 m<sup>2</sup> of the resulting PS plate per one liter of the developer, the developer was examined on whether insoluble compounds remained therein or not. The results thus obtained and the printing durability are summarized in the following Table 1.

40 In the following Table 1, the printing durability data are expressed in values relative to that observed in Comparative Example 1 which is assumed to be 100.

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Table 1

Insoluble Compounds Remaining in Developer and Printing Durability					
Ex. No.	Treatment A <sup>1)</sup>	Treatment B <sup>2)</sup>	Underlying Coating	Insoluble Compounds Remaining in Developer <sup>3)</sup>	Printing Durability (%)
1	Yes	Yes	No	A	95
2	Yes	Yes	Yes	A	120
3	Yes	Yes	No	A	100
4	Yes	Yes	Yes	A	120
1 *	No	No	No	B	100
2 *	Yes	No	No	A	40
3 *	Yes	No	Yes	A	60
4 *	Yes	No	No	A	40
5 *	Yes	No	Yes	A	60

\*: Comparative Example

1) Treatment with an alkali metal silicate.

2) Treatment with an aqueous sulfuric acid solution.

3) This is evaluated according to the following two stage evaluation criteria.

A: Any insoluble compounds was not formed.

B: A large amount of insoluble compounds was formed.

## Claims

1. A method for preparing a presensitized plate for use in making a lithographic printing plate comprising the steps of treating an-anodized aluminum plate with an aqueous solution of an alkali metal silicate having a pH ranging from 10 to 13 as determined at 25 °C, then treating the aluminum plate with an aqueous solution of an acid having a pH ranging from 1 to 6 and applying a light-sensitive layer onto the aluminum plate thus treated.
2. The method of claim 1 wherein a hydrophilic underlying coating layer is applied onto the aluminum plate after the treatment with the aqueous acid solution and prior to the application of the light-sensitive layer.
3. The method of claim 2 wherein the underlying coating layer is a hydrophilic layer comprising a compound having at least one amino group and at least one member selected from the group consisting of carboxyl group and groups in the form of salts thereof as well as sulfo group and groups in the form of salts thereof; a hydrophilic layer comprising a compound selected from the group consisting of those having at least one amino group and at least one hydroxyl group and salts thereof; a phosphate-containing hydrophilic layer; a hydrophilic layer comprising a polymeric compound having, in the molecule, repeating units derived from at least one monomer having a sulfo group; or an organic layer comprising at least one compound selected from the group consisting of substituted or unsubstituted aliphatic or aromatic compounds represented by the general formula:  $R^1(PO(OH)_2)_n$  or  $R^1(PO(OH)(R^2))_n$  (wherein n is 1 or 2; if n is 1, R<sup>1</sup> and R<sup>2</sup> each represents a substituted or unsubstituted alkyl, alkoxy, aryloxy, aryl, acyl or acyloxy group; and if n is 2, R<sup>1</sup> represents a substituted or unsubstituted alkylene or arylene group and R<sup>2</sup> is the same as that defined above).
4. The method of claim 1 wherein the concentration of the alkali metal silicate aqueous solution ranges from 2 to 15% by weight.
5. The method of claim 1 wherein the alkali metal silicate solution further comprises a hydroxide, an alkaline earth metal salt and/or a Group IVB metal salt.
6. The method of claim 5 wherein the amount of the alkaline earth metal salt and/or the Group IVB metal salt ranges from 0.05 to 5.0% by weight.

7. The method of claim 1 wherein the aqueous acid solution is an aqueous sulfuric acid, nitric acid, hydrochloric acid, oxalic acid or phosphoric acid solution.
- 5 8. The method of claim 1 wherein the light-sensitive layer is a member selected from the group consisting of those comprising o-quinonediazide compounds, those comprising diazide compounds and binders, those comprising azide compounds and polymeric binders, those comprising polyester compounds, those comprising polyvinyl cinnamate resins, those comprising photopolymerizable photopolymer compositions, and electrophotographic light-sensitive layers.
- 10 9. The method of claim 1 wherein the treatment with the alkali metal silicate aqueous solution is carried out by immersing the aluminum plate in the solution at a temperature ranging from 15 to 80 °C for 0.5 to 120 seconds.
- 15 10. The method of claim 1 wherein the treatment with the aqueous acid solution is carried out by immersing the aluminum plate in the solution at a temperature ranging from 10 to 70 °C for 0.5 to 120 seconds.

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54 **Method for preparing PS plate.**

57 A method for preparing a PS plate comprises the steps of treating an anodized aluminum plate with an aqueous solution of an alkali metal silicate having a pH ranging from 10 to 13 as determined at 25 °C, then treating the aluminum plate with an aqueous solution of an acid having a pH ranging from 1 to 6 and applying a light-sensitive layer onto the aluminum plate thus treated. The aluminum substrate of the PS plate is only slightly dissolved in an alkaline developer and this accordingly prevents the formation of insoluble compounds or sludge effectively, during development.

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## EUROPEAN SEARCH REPORT

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DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.5)
X	EP-A-0 089 510 (AMERICAN HOECHST CORPORATION) * page 9, line 19 - page 10, line 14; claims * * page 12, line 4 - line 10 * ---	1-10	B41N3/03
X,D	EP-A-0 149 490 (FUJI PHOTO FILM CO., LTD.,) * claim 1 * ---	3	
X,D	EP-A-0 110 417 (FUJI PHOTO FILM CO., LTD.,) ---	3	
P,X	EP-A-0 497 351 (FUJI PHOTO FILM CO., LTD.,) ---	3	
A	FR-A-2 202 308 (OCÉ-VAN DER GRINTEN N.V.) ---	1	
A,D	PATENT ABSTRACTS OF JAPAN vol. 014, no. 464 (M-1033)9 October 1990 & JP-A-02 185 493 (FUJI PHOTO FILM CO., LTD.,) * abstract * ---	1	
A	DE-B-11 18 009 (POLYCHROME CORP.) * claims * -----	1	
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 21 December 1993	Examiner Rasschaert, A
<b>CATEGORY OF CITED DOCUMENTS</b> X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ----- & : member of the same patent family, corresponding document			

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